

Theoretical Study of Reaction of Trifluoromethyl Radical with Hydroxyl and Hydrogen Radicals

HARUHIKO FUKAYA, TAIZO ONO, TAKASHI ABE

Chemistry Department, National Industrial Research Institute of Nagoya, Hirate-cho, Kita-ku, Nagoya 462, Japan

Received 2 July 1997; accepted 23 August 1997

ABSTRACT: *Ab initio* molecular orbital theory and density functional theory calculations have been carried out on the reactions of the trifluoromethyl radical with the hydroxyl and the hydrogen radicals. These reactions are key reactions that underlie a new fire extinguishing mechanism of non-bromine-containing halon replacements. The activation energies calculated by the MP2 and QCISD methods are in good agreement with the experimental values. The B3LYP, as well as MP2 and QCISD, give good results for the calculations of the heats of reactions. The GAUSSIAN-1 and GAUSSIAN-2 theory calculations present the most accurate results on both the activation energies and the heats of reactions. The effects of the scaling factors on the activation energies and the heats of reactions are also evaluated. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 277–289, 1998

Keywords: *ab initio* molecular orbital theory; density functional theory; ozone depletion problem; halon replacement; fire suppression mechanism

Introduction

The depletion of the stratospheric ozone is one of the most important global environmental problems. Chlorine or bromine atoms released from

chlorofluorocarbons (CFCs) or halons are thought to be a catalyst of ozone destruction.¹ The phase-out of CFCs by January 1, 1996 and halons by January 1, 1994 was decided in the International Copenhagen Agreement modification of the Montreal Protocol on Substances that Deplete the Ozone Layer.

Halons, perfluorinated carbons containing a bromine atom [e.g., CF₃Br (Halon 1301), CF₂BrCl (Halon 1211), CF₂BrCF₂Br (Halon 2402)], were considered ideal fire suppression agents because of their high efficiency, low toxicity, cleanliness, and

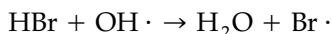
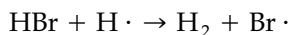
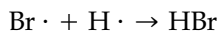
Correspondence to: H. Fukaya

Contract/grant sponsor: Environment Agency of Japan

This article includes Supplementary Material available from the authors upon request or via the internet at <ftp.wiley.com/public/journals/jcc/suppmat/19/277> or <http://journals.wiley.com/jcc/>

low electrical conductivity. The high fire extinguishing ability of halons is due to chemical suppression by removing free radicals from the combustion zone,^{2,3} whereas conventional fire fighting agents such as water and carbon dioxide suppress the fire only by a physical action (i.e., cooling and dilution).

Hydrogen atom and hydroxyl radicals are considered the main active species in the combustion reaction. Bromine atoms from halons convert them to relatively unreactive H_2 or H_2O molecules by the following catalytic cycle:



Bromine-containing compounds cannot be used as halon replacements in view of the ozone depletion problem, whereas non-bromine-containing compounds are not expected to have high fire suppression efficiency because of the lack of a chemical fire suppression mechanism in bromine atoms. We found, however, that several perfluoroalkylamines having no bromine atom showed a good fire extinguishing ability comparable to Halon 1301.^{4,5} This discovery prompted us to propose a new fire suppression mechanism for such non-bromine-containing perfluoroalkylamines in which the trifluoromethyl radical mimics the fire extinguishing role played by the bromine atom.⁶

We report here *ab initio* molecular orbital theory and density functional theory (DFT) calculations on the reactions of the trifluoromethyl radical with the hydroxyl or the hydrogen radical, which are constituents of our proposed trifluoromethyl radical-mediated fire suppression mechanism. A part of the reactions we describe here have also been studied from a viewpoint of the decomposition of hydrofluorocarbons in the atmosphere.⁷

Computational Methods

Ab initio and DFT calculations were performed with the GAUSSIAN-92⁸ or -94⁹ program. Three basis sets, 6-31G(d, p), 6-311G(2d, 2p), and 6-311 + G(3df, 3pd), were used for assessing the effect of the extension of the valence space, diffuse functions, and correlation space.¹⁰ Geometry optimizations and calculations of zero-point energies were performed by the following methods: Hartree-Fock self-consistent field (HF); second-order Møller-Plesset perturbation theory (MP2)¹¹;

quadratic configuration interaction including single and double substitutions (QCISD); Becke's exchange¹² with the Vosko-Wilk-Nusair correlation functional¹³ (BVWN); Becke's exchange with the Lee-Yang-Parr correlation functional¹⁴ (BLYP); and Becke's three-parameter exchange¹⁵ with the Lee-Yang-Parr correlation functional (B3LYP). The MP4/6-311G(d, p), MP4/6-311 + G(d, p), MP4/6-311G(2df, p), QCISD(T)/6-311G(d, p) and MP2/6-311 + G(3df, 2p) energies were also evaluated on MP2(FU)/6-31G(d) geometries for the GAUSSIAN-1¹⁶ and GAUSSIAN-2¹⁷ theory calculations.

Results and Discussion

We investigated the following reactions on the trifluoromethyl radical and its related species that are included in the fire suppression process¹⁸:

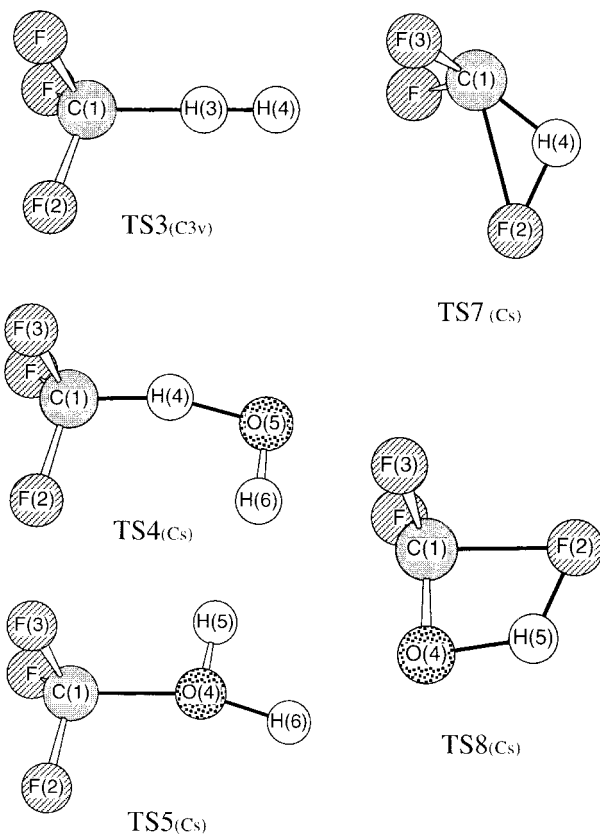
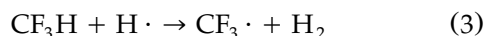
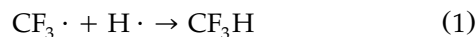
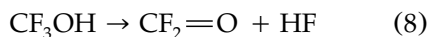
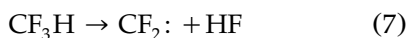
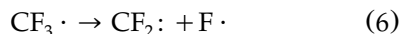
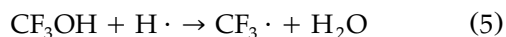
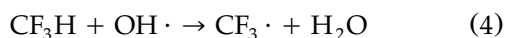


FIGURE 1. Notations of the transition states.



Reactions (1) and (2) are trifluoromethyl radical-mediated scavenging processes of the hydrogen and the hydroxyl radicals. Reactions (3), (4), and (5) are regenerations of the trifluoromethyl radicals; and reactions (6), (7), and (8) represent

the decomposition of the trifluoromethyl radical and the products formed in reactions (1) and (2).

Transition states were found in reactions (3), (4), (5), (7), and (8), respectively (Fig. 1). The *ab initio*-optimized geometries of these transition states are summarized in Table I. On the geometries of the stable species, no significant difference appeared in the variation of the basis sets, 6-31G(d,p) [BS1], 6-311G(2d,2p) [BS2], and 6-311 + G(3df,3pd) [BS3]. On the other hand, the optimized geometries of transition states are affected by the basis sets: The C1—H4—O5 bond angle of

TABLE I.
Optimized Geometries Calculated by *Ab Initio* Methods.

Species	Coordinate	HF			MP2			QCISD		MP2(FU)	
		BS1 ^a	BS2 ^a	BS3 ^a	BS1 ^a	BS2 ^a	BS3 ^a	BS1 ^a	BS2 ^a	6-31G*	Expl. ^b
Bond length (Å)											
CF ₃ ·	CF	1.301	1.293	1.290	1.329	1.319	1.313	1.328	1.317	1.327	1.33
CF ₃ H	CH	1.077	1.075	1.077	1.086	1.082	1.085	1.087	1.083	1.089	1.098
	CF	1.317	1.311	1.308	1.344	1.336	1.332	1.343	1.333	1.343	1.333
OH·	OH	0.955	0.949	0.951	0.972	0.965	0.966	0.975	0.967	0.979	0.971
CF ₃ OH	CO	1.330	1.328	1.328	1.351	1.347	1.343	1.351	1.347	1.350	
	CF	1.305	1.299	1.296	1.332	1.324	1.319	1.331	1.321	1.330	
	CF'	1.321	1.314	1.312	1.352	1.343	1.339	1.349	1.339	1.351	
	OH	0.946	0.942	0.943	0.966	0.960	0.962	0.965	0.958	0.974	
H ₂	HH	0.733	0.734	0.734	0.734	0.737	0.737	0.738	0.742	0.738	0.741
H ₂ O	OH	0.943	0.940	0.940	0.961	0.957	0.959	0.961	0.955	0.969	0.958 ^c
CF=O	CO	1.157	1.150	1.150	1.187	1.176	1.175	1.183	1.171	1.186	1.174
	CF	1.290	1.284	1.280	1.328	1.319	1.312	1.324	1.314	1.326	1.312
HF	HF	0.901	0.896	0.897	0.921	0.915	0.917	0.920	0.913	0.934	0.917
CF ₂ :	CF	1.283	1.273	1.269	1.314	1.302	1.295	1.317	1.302	1.313	1.300
TS3	C1F2	1.306	1.298	1.296	1.334	1.324	1.319	1.333	1.322	1.332	
	C1H3	1.378	1.381	1.382	1.393	1.395	1.409	1.379	1.378	1.423	
	H3H4	0.913	0.907	0.911	0.880	0.877	0.871	0.903	0.905	0.879	
TS4	C1F2	1.309	1.302	1.299	1.341	1.332	1.325	1.338	1.327	1.339	
	C1F3	1.304	1.297	1.294	1.334	1.325	1.319	1.332	1.322	1.332	
	C1H4	1.322	1.318	1.316	1.224	1.216	1.216	1.266	1.259	1.243	
	H4O5	1.160	1.162	1.171	1.240	1.246	1.246	1.210	1.216	1.229	
	O5H6	0.951	0.947	0.948	0.972	0.966	0.967	0.972	0.966	0.979	
TS5	C1F2	1.295	1.288	1.285	1.325	1.315	1.308	1.323	1.311	1.324	
	C1F3	1.307	1.298	1.295	1.339	1.327	1.319	1.335	1.323	1.337	
	C1O4	1.730	1.725	1.717	1.676	1.668	1.654	1.703	1.697	1.695	
	O4H5	0.952	0.947	0.948	0.974	0.968	0.972	0.972	0.965	0.981	
	O4H6	1.287	1.279	1.263	1.203	1.188	1.163	1.263	1.256	1.214	
TS7	C1F2	1.905	1.960	2.008	1.905	1.927	1.965	1.914	1.941	1.927	
	C1F3	1.263	1.249	1.242	1.299	1.285	1.275	1.298	1.283	1.297	
	C1H4	1.179	1.173	1.165	1.211	1.205	1.201	1.199	1.193	1.223	
	F2H4	1.235	1.263	1.289	1.196	1.216	1.231	1.219	1.238	1.197	
TS8	C1F2	1.734	1.772	1.789	1.720	1.731	1.742	1.731	1.745	1.718	
	C1F3	1.276	1.263	1.258	1.317	1.304	1.296	1.312	1.297	1.315	
	C1O4	1.241	1.238	1.237	1.263	1.258	1.255	1.263	1.257	1.262	
	F2H5	1.176	1.209	1.217	1.180	1.203	1.202	1.177	1.201	1.192	
	O4H5	1.194	1.162	1.154	1.235	1.213	1.208	1.229	1.203	1.254	

TABLE I.
(Continued)

Species	Coordinate	HF			MP2			QCISD		MP2(FU)	
		BS1 ^a	BS2 ^a	BS3 ^a	BS1 ^a	BS2 ^a	BS3 ^a	BS1 ^a	BS2 ^a	6-31G*	Expl. ^b
Bond angle (degrees)											
CF ₃ ·	FCF	111.3	111.4	111.4	111.2	111.3	111.3	111.2	111.3	111.2	112
CF ₃ H	HCF	110.5	110.5	110.5	110.4	110.3	110.4	110.5	110.4	110.5	110.3
	FCF	108.4	108.5	108.5	108.5	108.6	108.5	108.4	108.5	108.5	108.6
CF ₃ OH	OCF	108.9	108.8	108.7	108.3	108.3	108.3	108.4	108.4	108.3	
	OCF'	111.9	112.0	112.0	112.2	112.2	112.2	112.1	112.1	112.2	
	FCF'	108.6	108.6	108.6	108.8	108.7	108.7	108.8	108.7	108.8	
	F'CF'	106.7	106.8	106.9	106.5	106.6	106.6	106.6	106.7	106.5	
	COH	110.5	110.2	110.7	108.1	108.1	108.5	108.3	108.3	108.2	
H ₂ O	HOH	106.0	105.6	106.3	103.8	103.3	104.1	104.0	103.6	104.0	104.5 ^c
CF=O	OCF	125.9	125.8	125.8	126.3	126.2	126.2	126.1	126.0	126.3	126.1
CF ₂ :	FCF	104.5	105.0	105.2	104.2	104.9	105.0	104.1	104.7	104.3	104.9
TS3	F2C1H3	108.8	108.7	108.7	108.9	108.6	108.6	108.9	108.7	108.8	
TS4	F2C1F3	109.9	110.0	110.1	109.4	109.7	109.9	109.6	109.8	109.5	
	F2C1H4	108.3	108.7	108.9	108.6	108.9	109.1	108.3	108.7	108.4	
	F3C1H4	109.2	108.9	108.7	109.7	109.3	109.2	109.6	109.2	109.6	
	C1H4O5	169.5	171.9	174.1	162.5	166.9	170.4	165.2	169.1	163.1	
	H4O5H6	101.4	100.7	101.1	99.2	98.2	98.9	99.5	98.6	100.1	
TS5	F2C1F3	110.4	110.5	110.7	109.8	110.0	110.3	110.2	110.4	109.8	
	F2C1O4	104.5	104.3	104.0	103.9	103.9	103.5	104.2	104.3	103.7	
	F3C1O4	110.9	110.8	110.6	112.0	111.6	111.3	111.4	111.1	112.0	
	C1O4H5	99.8	99.8	100.9	101.6	102.4	105.4	100.5	100.8	101.1	
	C1O4H6	165.6	165.8	164.3	161.3	160.5	155.9	163.6	163.8	161.3	
	H5O4H6	94.6	94.3	94.8	97.1	97.1	98.7	95.9	95.4	97.6	
TS7	F2C1F3	106.8	108.0	108.9	105.0	105.5	106.1	105.3	106.0	104.9	
	F3C1H4	122.4	122.5	122.5	121.4	121.5	121.4	121.6	121.8	121.1	
	C1F2H4	36.9	34.9	33.1	37.9	37.0	35.6	37.3	36.3	37.7	
	C1H4F2	104.2	107.1	109.7	104.7	105.6	107.8	104.7	105.9	105.5	
	F2C1H4	39.0	38.0	37.2	37.4	37.4	36.6	38.0	37.9	36.8	
TS8	F2C1F3	102.7	102.6	102.3	103.4	103.5	103.2	103.3	103.3	103.3	
	O4C1F3	122.1	122.1	122.2	121.8	121.7	121.9	121.9	121.8	121.8	
	C1F2H5	63.5	61.9	61.3	63.9	63.3	62.9	63.9	63.1	65.2	
	F2H5O4	125.6	126.6	127.1	125.6	125.4	125.8	125.8	125.9	123.0	
	F2C1O4	88.6	87.6	87.1	90.8	90.4	90.0	90.0	89.4	91.1	
	C1O4H5	82.3	84.0	84.5	79.7	80.9	81.3	80.4	81.7	80.7	

^aBS1, BS2, and BS3 are 6-31G(d, p), 6-311G(2d, 2p), and 6-311 + + G(3df, 3pd), respectively.

^bRef. 19 unless otherwise noted.

^cRef. 20.

TS4 neared 180° with extended basis sets, and the changes in the angle caused by the changes of the basis set from BS1 to BS2 and from BS2 to BS3 were 2.4° and 2.2° for HF, 4.4° and 3.5° for MP2, and 3.8° for QCISD, respectively. In the optimized geometries of TS5, a significant difference appeared between MP2/BS2 and MP2/BS3; that is, the change in the O4—H6 bond length was −0.025 Å, and the changes in the C1—O4—H5 and the C1—O4—H6 bond angle were 3.0° and −4.6°, respectively.

In TS7 and TS8, which have cyclic structures, more significant differences were observed in the geometries by the change of the basis set. For example, the changes in the C1—F2 bond length of TS7 are the largest in Table I; that is, those between BS1 and BS2 and between BS2 and BS3 were 0.055 Å and 0.048 Å for HF, 0.022 Å and 0.038 Å for MP2, and 0.027 Å for QCISD, respectively. Other geometrical data such as F2—H4, C1—F3, C1—H4—F2, and C1—F2—H4 were also affected by the basis sets used. In TS8, the changes in the

C1—F2 bond length were also large; that is, those found between BS1 and BS2 and between BS2 and BS3 were 0.038 Å and 0.017 Å for HF, 0.011 Å and 0.011 Å for MP2, and 0.014 Å for QCISD, respectively. Other geometrical data such as F2—H5, O4—H5, C1—F3, C1—O4—H5, and C1—F2—H5 showed large changes between BS1 and BS2, but they showed only small changes between BS2 and BS3.

For the stable species, the differences in the optimized geometries obtained by the DFT methods were also small in all the basis sets used

(Table II). We failed to locate a transition state of reaction (4) by the BLYP method. In this reaction, the energy just decreased with the reaction coordinate of “CF₃H + OH” to “CF₃ + H₂O” (Fig. 2). In TS3, large geometry changes were found between BS1 and BS2 in all DFT methods: that is, for C1—H3 bond length, 0.013 Å (BVWN), 0.018 Å (BLYP), and 0.013 Å (B3LYP); for H3—H4 bond length, −0.024 Å (BVWN), −0.024 Å (BLYP), and −0.017 Å (B3LYP). In TS4, not only the C1—H4—O5 bond angle but also the H4—O5 bond length was affected by the basis sets. In TS5,

TABLE II.
Optimized Geometries Calculated by DFT Methods.

Molecule	Coordinate	BVWN			BLYP			B3LYP		
		BS1 ^a	BS2 ^a	BS3 ^a	BS1 ^a	BS2 ^a	BS3 ^a	BS1 ^a	BS2 ^a	BS3 ^a
Bond length (Å)										
CF ₃ ·	CF	1.347	1.342	1.339	1.345	1.341	1.338	1.327	1.322	1.319
CF ₃ H	CH	1.095	1.088	1.088	1.102	1.096	1.095	1.094	1.089	1.089
	CF	1.362	1.360	1.359	1.359	1.358	1.358	1.342	1.339	1.338
OH·	OH	0.986	0.979	0.979	0.991	0.985	0.985	0.980	0.974	0.974
CF ₃ OH	CO	1.367	1.362	1.360	1.366	1.362	1.360	1.351	1.347	1.346
	CF	1.350	1.347	1.345	1.348	1.345	1.344	1.331	1.328	1.326
	CF'	1.373	1.372	1.371	1.370	1.369	1.369	1.351	1.348	1.347
H ₂	OH	0.973	0.969	0.969	0.979	0.974	0.975	0.968	0.964	0.965
	HH	0.737	0.737	0.737	0.747	0.747	0.747	0.743	0.743	0.743
H ₂ O	OH	0.971	0.966	0.966	0.976	0.971	0.971	0.965	0.961	0.961
CF ₂ =O	CO	1.191	1.180	1.179	1.193	1.182	1.181	1.180	1.170	1.170
	CF	1.345	1.342	1.340	1.342	1.340	1.339	1.322	1.319	1.317
HF	HF	0.932	0.926	0.928	0.937	0.931	0.933	0.925	0.920	0.922
CF ₂ ·	CF	1.337	1.329	1.324	1.335	1.326	1.322	1.313	1.305	1.301
TS3	C1F2	1.353	1.349	1.348	1.350	1.347	1.346	1.332	1.327	1.326
	C1H3	1.291	1.304	1.311	1.349	1.367	1.375	1.368	1.381	1.385
	H3H4	1.005	0.981	0.975	0.964	0.940	0.935	0.930	0.913	0.913
TS4	C1F2	1.359	1.356	1.353	— ^a	— ^a	— ^a	1.339	1.334	1.332
	C1F3	1.354	1.350	1.348	— ^a	— ^a	— ^a	1.332	1.328	1.326
	C1H4	1.192	1.202	1.200	— ^a	— ^a	— ^a	1.229	1.228	1.223
	H4O5	1.386	1.356	1.373	— ^a	— ^a	— ^a	1.281	1.277	1.297
	O5H6	0.982	0.976	0.976	— ^a	— ^a	— ^a	0.976	0.971	0.971
TS5	C1F2	1.337	1.333	1.330	1.336	1.332	1.330	1.320	1.315	1.312
	C1F3	1.353	1.349	1.346	1.351	1.347	1.345	1.333	1.328	1.325
	C1O4	1.695	1.689	1.672	1.704	1.696	1.676	1.694	1.687	1.671
	O4H5	0.979	0.974	0.974	0.985	0.980	0.981	0.974	0.970	0.970
	O4H6	1.329	1.334	1.336	1.308	1.314	1.319	1.275	1.275	1.272
TS7	C1F2	2.012	2.046	2.088	1.992	2.020	2.065	1.943	1.975	2.016
	C1F3	1.314	1.305	1.298	1.314	1.306	1.298	1.295	1.286	1.279
	C1H4	1.192	1.189	1.181	1.211	1.206	1.195	1.206	1.201	1.193
	F2H4	1.258	1.274	1.298	1.238	1.256	1.282	1.220	1.239	1.261
TS8	C1F2	1.791	1.821	1.845	1.773	1.800	1.826	1.745	1.772	1.793
	C1F3	1.332	1.324	1.319	1.331	1.324	1.319	1.312	1.303	1.299
	C1O4	1.275	1.269	1.267	1.275	1.270	1.268	1.261	1.256	1.255
	F2H5	1.235	1.268	1.280	1.223	1.257	1.269	1.195	1.227	1.237
	O4H5	1.211	1.185	1.174	1.229	1.202	1.191	1.226	1.199	1.189

TABLE II.
(Continued)

Molecule	Coordinate	BVWN			BLYP			B3LYP		
		BS1 ^a	BS2 ^a	BS3 ^a	BS1 ^a	BS2 ^a	BS3 ^a	BS1 ^a	BS2 ^a	BS3 ^a
Bond angle (degree)										
CF ₃ ·	FCF	111.2	111.2	111.4	111.1	111.1	111.3	111.2	111.2	111.4
CF ₃ H	HCF	110.3	110.3	110.4	110.4	110.4	110.4	110.4	110.4	110.5
	FCF	108.6	108.6	108.6	108.6	108.6	108.5	108.5	108.5	108.5
CF ₃ OH	OCF	108.2	108.4	108.4	108.1	108.2	108.4	108.4	108.5	108.5
	OCF'	112.3	112.4	112.4	112.3	112.5	112.5	112.2	112.3	112.3
	FCF'	108.7	108.6	108.5	108.8	108.6	108.5	108.7	108.6	108.6
	F'CF'	106.5	106.3	106.4	106.5	106.4	106.3	106.5	106.5	106.5
	COH	108.0	108.3	109.1	107.9	108.1	109.1	108.7	108.7	109.6
H ₂ O	HOH	103.0	103.4	104.5	102.7	103.2	104.5	103.7	104.0	105.1
CF=O	OCF	126.2	126.3	126.3	126.2	126.3	126.3	126.1	126.1	126.1
CF ₂ :	FCF	104.1	104.4	104.7	103.9	104.3	104.6	104.1	104.6	104.8
TS3	F2C1H3	109.2	109.1	109.1	109.1	108.9	109.0	108.9	108.8	108.8
TS4	F2C1F3	109.4	109.6	109.6	— ^a	— ^a	— ^a	109.5	109.6	109.7
	F2C1H4	109.4	109.5	109.6	— ^a	— ^a	— ^a	108.9	109.2	109.5
	F3C1H4	109.4	109.2	109.1	— ^a	— ^a	— ^a	109.5	109.2	109.0
	C1H4O5	170.7	172.8	176.0	— ^a	— ^a	— ^a	166.6	170.1	173.6
	H4O5H6	100.8	100.6	101.9	— ^a	— ^a	— ^a	100.3	100.0	101.1
TS5	F2C1F3	110.3	110.3	110.4	110.2	110.3	110.3	110.3	110.4	110.4
	F2C1O4	104.6	104.6	104.6	104.2	104.4	104.3	104.2	104.3	104.2
	F3C1O4	111.1	111.0	110.9	111.2	111.1	111.1	111.2	111.1	110.9
	C1O4H5	102.2	102.4	103.6	102.0	102.4	103.7	101.9	102.3	103.7
	C1O4H6	161.1	161.1	159.6	160.7	160.5	158.8	161.1	160.9	159.0
TS7	H5O4H6	96.7	96.5	96.8	97.2	97.1	97.5	96.9	96.8	97.3
	F2C1F3	106.5	107.0	107.7	106.0	106.3	107.2	105.7	106.2	106.9
	F3C1H4	121.6	121.6	121.6	121.4	121.5	121.5	121.5	121.6	121.6
	C1F2H4	33.8	32.5	30.9	35.1	34.0	32.2	36.6	35.3	33.7
	C1H4F2	110.4	112.3	114.7	108.9	110.3	112.9	106.4	108.0	110.5
TS8	F2C1H4	35.9	35.2	34.4	36.0	35.7	34.9	37.0	36.6	35.9
	F2C1F3	104.3	104.3	104.2	104.0	104.1	104.0	103.5	103.6	103.4
	O4C1F3	121.8	121.9	122.1	121.8	121.9	122.1	121.8	121.9	122.1
	C1F2H5	62.4	61.4	60.8	63.1	62.3	61.7	63.7	62.7	62.1
	F2H5O4	126.2	126.1	126.4	125.5	125.3	125.6	125.2	125.2	125.6
	F2C1O4	89.1	88.2	87.4	89.8	88.9	88.1	89.8	89.0	88.3
	C1O4H5	82.3	84.3	85.3	81.6	83.5	84.7	81.3	83.1	83.9

^aBS1, BS2, and BS3 are 6-31G(d, p), 6-311G(2d, 2p), and 6-311 + + G(3df, 3pd), respectively.
^bCould not locate transition state.

moderate geometry changes were found between BS2 and BS3 in the C1—O4 bond length and the C1—O4—H5 and the H5—O4—H6 bond angles.

In the DFT methods, as well as *ab initio*, the geometries of TS7 and TS8 were affected considerably by the basis sets. Changes in bond lengths as large as 0.04 Å were observed in the C1—F2 of TS7 between BS2 and BS3 for BLYP and B3LYP.

For the stable species, the optimized geometries obtained by the MP2, QCISD, and B3LYP methods

were very similar to the experimental one, whereas the HF method underestimated bond length by about 0.02–0.04 Å. The BVWN and BLYP methods gave longer a bond length for the C—F bond by about 0.02–0.04 Å. For the transition state, however, the optimized geometries differed from method to method. In the six methods investigated, MP2 and QCISD gave structures similar to one another, with maximal differences of 0.059 Å (BS1) and 0.067 Å (BS2) in the O4—H6 bond length

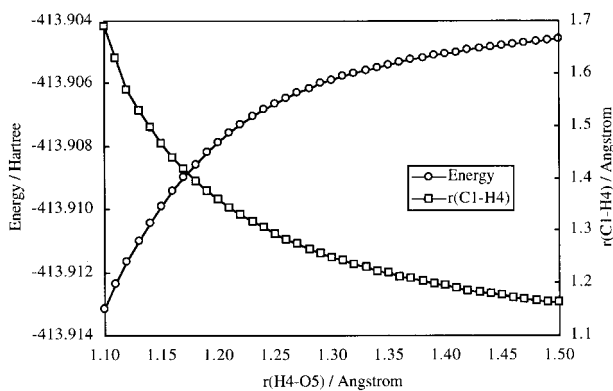


FIGURE 2. Energy change of reaction (4) calculated at the BLYP/6-31G** level.

of TS5. In the HF method, taking account of giving shorter bond length (mentioned previously), the bond lengths longer than those of MP2 or QCISD is significant: H3—H4 for TS3, C1—H4 for TS4, C1—O4 and O4—H6 for TS5, F2—H4 for TS7, and C1—F2 for TS8.

The optimized geometries of the transition states determined by the DFT methods, especially BVWN, were significantly different from the MP2 or QCISD geometries. The largest changes from MP2 geometries were observed in the H4—O5 bond length of TS4 and the O4—H6 bond of TS5 obtained by BVWN.

The electronic energies obtained by *ab initio* and DFT methods, respectively, are shown on the Supplementary Material web site.²¹ Tables III shows zero-point energy corrections (thermal energy corrections are shown on Supplementary Material web site²¹). The frequency calculations of some species at the MP2/BS3 and QCISD/BS2 levels could not be performed for technical reasons. For these species, we used the corrections calculated by the smaller basis sets; that is, MP2/BS2 instead of MP2/BS3, and QCISD/BS1 instead of QCISD/BS2. As shown in Table III, the differences of correction were less than 0.1 millihartree (0.06 kcal/mol), regardless of the basis set used, so the effects of using the corrections calculated by the smaller basis sets for MP2/BS3 and QCISD/BS2 were negligible.

Table IV shows the scaling factors for zero-point vibrational energies from recent studies.^{22–24} Because not all scaling factors were available for the method used, we utilized the scaling factors shown in Table V as alternatives by choosing the values

which are used in the basis sets closest to those we used. Table V shows the activation energy of reactions (3), (4), (5), (7), and (8) calculated by the *ab initio* and DFT methods. The activation energies calculated at the QCISD/BS2 level were most consistent with the experimental values, although they overestimated by about 3 kcal/mol. Those calculated by the MP2 method also approximated the experimental ones, and the larger basis set gave better results in both methods. The HF method overestimated by about 10–25 kcal/mol and only a small improvement was attained by using larger basis sets. All DFT methods underestimated by about 4–9 kcal/mol.

Table VI shows the heats of reactions calculated by the *ab initio* and DFT methods. The experimental values were calculated from the experimental data on the heats of formations at 298.15 K.^{19,25,26} The heats of reactions obtained by the DFT methods, especially B3LYP, were consistent with the experimental values, as well as QCISD and MP2. The HF method gave still poorer results.

The scaling factors varied with the method and slightly with the basis set as shown in Table IV. To verify the effect of using arbitrary scaling factors, the corrections for the activation energy and the reaction enthalpy are summarized in Tables VII and VIII, respectively. Both corrections were not so affected by the methods, but differed from reaction to reaction. Regarding the activation energy, reaction (5) was slightly affected by the correction, whereas reaction (7) was significantly affected, up to about 4–5 kcal/mol. The errors in activation energies caused by the scale factor's error, however, would become only 0.4–0.5 kcal/mol for reaction (7), even if the error of the scale factor had been 0.1. On the heats of reactions, almost no influence by the corrections was observed in reaction (4) and only a small influence in reaction (3). The enthalpy of reaction (1) was the most affected case—that is, twice as much as the activation energy of reaction (7). But the maximal error may have been less than 1 kcal/mol.

Table IX shows the results of GAUSSIAN-1 (G1) and GAUSSIAN-2 (G2) theory calculations of stable and transition-state species. The geometries used for this calculation, optimized at the MP2(FU)/6-31G* level, are summarized in Table I. The higher polarization functions' correction, $\Delta E(2df)$, in fluorine-containing species, were very large. The activation energies and the heats of reactions calculated at the MP4/6-311G**(2df)/MP2(FU)/6-31G* level, however,

TABLE III.
The Zero-Point Vibrational Energies.^a

Species	HF			MP2			QCISD			B3LYP			B3LYP		
	BS1	BS2	BS3	BS1	BS2	BS3	BS1	BS2	BS3	BS1	BS2	BS3	BS1	BS2	BS3
CF ₃ ·	13.56	13.50	13.55	12.44	12.34	— ^b	12.48	12.44	11.16	11.38	11.19	11.16	11.46	11.25	11.20
CF ₃ H	27.99	27.77	27.70	26.19	25.89	— ^b	26.24	25.99	23.99	24.46	24.15	23.99	24.34	24.00	23.82
OH·	9.24	9.25	9.25	8.76	8.73	8.75	8.61	8.61	8.26	8.18	8.22	8.26	8.06	8.10	8.14
CF ₃ OH	32.11	32.03	31.99	29.64	29.45	— ^b	29.89	— ^b	27.29	27.65	27.42	27.29	27.58	27.35	27.16
H ₂	10.56	10.46	10.45	10.50	10.32	10.30	10.27	10.05	10.15	10.25	10.16	10.15	10.01	9.91	9.90
H ₂ O	23.19	23.15	23.11	21.88	21.75	21.64	21.87	21.81	20.91	20.85	20.89	20.91	20.59	20.62	20.64
F ₂ C=O	15.79	15.74	15.75	14.14	14.09	— ^b	14.32	14.33	13.14	13.33	13.20	13.14	13.37	13.22	13.14
HF	10.24	10.26	10.23	9.56	9.58	9.51	9.55	9.62	9.09	9.05	9.11	9.09	8.93	9.00	8.99
CF ₂ ·	7.78	7.75	7.77	7.11	7.03	7.04	7.05	7.03	6.28	6.41	6.31	6.28	6.48	6.38	6.33
TS3	24.09	23.78	23.85	23.24	22.87	— ^b	22.97	22.66	21.34	21.72	21.34	21.34	21.64	21.29	21.25
TS4	32.97	32.92	32.93	31.35	31.05	— ^b	30.95	— ^b	29.75	30.38	29.71	29.75	— ^c	— ^c	— ^c
TS5	32.28	32.17	32.31	30.91	30.63	— ^b	30.38	— ^b	27.83	28.10	27.81	27.83	28.05	27.70	27.67
TS7	20.48	20.39	20.44	18.93	18.75	18.76	18.92	18.80	17.52	17.68	17.40	17.52	17.54	17.27	17.36
TS8	25.87	25.63	25.54	24.02	23.76	— ^b	24.12	23.94	21.93	22.39	22.10	21.93	22.44	22.12	21.89

^aThe energies are given in millihartrees.
^bCould not calculate.
^cCould not locate transition state.

TABLE IV.
Scaling Factors for Zero-Point Energies.

Method	Scale factor	Ref.
HF / 6-31G(d, p)	0.9181	22
HF / 6-311G(d, p)	0.9248	22
HF / 6-311G(df, p)	0.9247	22
MP2 / 6-31G(d, p)	0.9608	22
QCISD / 6-31G(d)	0.9776	22
BVWN / 6-31G(d)	0.9985	23
BLYP / 6-31G(d)	1.0126	22
BLYP / 6-31G(d)	1.0119	23
BLYP / 6-311G(df, p)	1.0167	22
B3LYP / 6-31G(d)	0.9806	22
B3LYP / 6-31G(d)	0.9804	23
B3LYP / 6-31G(d)	0.98	24
B3LYP / 6-311 + G(3df, 2p)	0.989	24

were not so different from those calculated by other methods, because the effects of the corrections between the reactants and the transition states, or between the reactants and the products, canceled each other (Table X). The single-point calculations by the individual methods needed for the G1 and G2 procedures showed good results, especially the QCISD/6-311G**//MP2(FU)/6-31G* method for the activation energy, and the

MP4/6-311 + G**//MP2(FU)/6-31G* method for heats of reaction. The G1 and G2 theory calculations, however, gave the best results among all methods we tested.

Conclusions

The optimized geometries of the transition states are affected by the basis sets, whereas those of the stable species are not similarly affected. For the stable species, the MP2, QCISD, and B3LYP methods gave similar geometries to the experimental ones. For the transition states, the optimized geometries differed from method to method.

The activation energies calculated by the MP2 and QCISD methods were consistent with the experimental values, and the use of larger basis sets improved them. The DFT methods underestimated the activation energies by about 4–9 kcal/mol, and the HF method overestimated them by about 10–25 kcal/mol.

The heats of reactions obtained by the DFT methods, especially B3LYP, were consistent with the experimental values, as well as QCISD and MP2.

TABLE V.
Scaling Factors Used and Activation Energies.^a

Method	Basis set	Scale factor	Reaction 3	Reaction 4	Reaction 5	Reaction 7	Reaction 8
HF	BS1	0.918	25.2	30.3	63.2	92.0	58.6
	BS2	0.925	24.8	29.5	62.8	89.2	58.3
	BS3	0.925	24.7	29.5	61.6	87.7	58.1
MP2	BS1	0.961	20.9	11.3	52.8	78.2	43.4
	BS2	0.961	19.1	9.3	50.3	75.8	43.3
	BS3	0.961	19.0	8.7	47.4	74.0	42.9
QCISD	BS1	0.978	17.3	11.0	46.7	78.5	47.2
	BS2	0.978	14.8	9.1	44.4	76.8	47.6
BVWN	BS1	0.999	3.4	−2.2	27.0	62.0	34.4
	BS2	0.999	4.3	−2.1	26.7	60.0	34.5
	BS3	0.999	4.8	−0.6	25.8	58.6	34.8
BLYP	BS1	1.012	2.9	— ^b	26.4	62.2	33.4
	BS2	1.017	4.1	— ^b	25.9	60.1	33.6
	BS3	1.017	4.8	— ^b	24.9	58.6	34.0
B3LYP	BS1	0.980	6.4	−0.9	33.8	71.1	40.0
	BS2	0.980	7.2	−0.8	33.2	69.0	40.2
	BS3	0.989	7.6	0.5	31.9	67.5	40.4
Experimental			10.9–12.8 ^c	4.6–6.1 ^d			

^aThe energies are given in kilocalories per mole.

^bCould not locate transition state.

^cCalculated from the activation energy of the reverse reaction in ref. 27 and the heat of reaction in Table VI.

^dRef. 28.

TABLE VI.
Heats of Reactions at 298.15 K.^a

Method	Basis set	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5	Reaction 6	Reaction 7	Reaction 8
HF	BS1	−82.6	−81.0	4.8	4.3	2.7	63.2	59.3	15.3
	BS2	−82.3	−79.5	5.5	3.4	0.6	61.8	55.0	9.6
	BS3	−81.7	−78.9	4.8	1.4	−1.3	63.8	54.2	9.2
MP2	BS1	−100.6	−118.1	6.6	−10.7	6.8	88.2	64.2	12.1
	BS2	−102.3	−118.6	7.0	−13.1	3.2	87.8	58.7	6.2
	BS3	−103.9	−120.5	7.4	−16.2	0.4	91.9	57.9	5.8
QCISD	BS1	−101.5	−109.5	2.8	−6.0	1.9	79.1	59.9	13.9
	BS2	−103.1	−109.1	2.7	−7.6	−1.6	77.7	54.6	7.9
BVWN	BS1	−103.0	−104.8	−8.3	−11.3	−9.5	83.4	56.5	4.7
	BS2	−103.2	−102.8	−6.8	−12.6	−13.0	80.6	50.0	−2.6
	BS3	−103.3	−100.5	−6.6	−14.2	−17.0	80.5	46.9	−5.7
BLYP	BS1	−100.1	−110.3	−3.7	−12.2	−2.0	89.9	62.4	11.8
	BS2	−99.9	−108.1	−2.4	−13.8	−5.5	86.5	55.1	4.2
	BS3	−100.1	−104.9	−2.0	−15.4	−10.6	85.6	50.8	0.1
B3LYP	BS1	−102.9	−111.4	−1.7	−9.3	−0.8	88.6	65.2	15.2
	BS2	−102.8	−109.4	−0.4	−10.7	−4.1	85.7	58.5	8.0
	BS3	−102.6	−107.0	−0.4	−12.6	−8.3	85.6	55.2	4.9
Experimental ^b		−106.3	−117.6	2.1	−12.9	−1.6	82–88	53–58	2.9

^aThe energies are given in kilocalories per mole and the same scale factors are used in Table V.
^bCalculated by the heat of formation at 298.15 K in ref. 19, except for CF₃OH; that for CF₃OH is taken from ref. 25; that for CF₂: is taken from both refs. 19 and 26.

TABLE VII.
Effect of Zero-Point Energy on Activation Energies.^a

Method	Basis set	Reaction 3	Reaction 4	Reaction 5	Reaction 7	Reaction 8
HF	BS1	−2.5	−2.7	0.1	−4.7	−3.9
	BS2	−2.5	−2.6	0.1	−4.6	−4.0
	BS3	−2.4	−2.5	0.2	−4.6	−4.1
MP2	BS1	−1.9	−2.3	0.8	−4.6	−3.5
	BS2	−1.9	−2.2	0.7	−4.5	−3.6
	BS3	−1.9	−2.3	0.7	−4.5	−3.6
QCISD	BS1	−2.0	−2.4	0.3	−4.6	−3.6
	BS2	−2.1	−2.3	0.3	−4.5	−3.7
BVWN	BS1	−1.7	−1.4	0.3	−4.3	−3.3
	BS2	−1.8	−1.7	0.2	−4.2	−3.3
	BS3	−1.7	−1.6	0.3	−4.1	−3.4
BLYP	BS1	−1.7	— ^b	0.3	−4.3	−3.2
	BS2	−1.7	— ^b	0.2	−4.2	−3.3
	BS3	−1.6	— ^b	0.3	−4.1	−3.3
B3LYP	BS1	−1.8	−2.3	0.4	−4.4	−3.4
	BS2	−1.8	−2.1	0.4	−4.3	−3.4
	BS3	−1.7	−2.1	0.4	−4.2	−3.5

^aThe energies are given in kilocalories per mole.
^bCould not locate transition state.

TABLE VIII.
Effect of Thermal Energy Correction on Heats of Reactions.^a

Method	Basis set	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5	Reaction 6	Reaction 7	Reaction 8
HF	BS1	9.1	4.9	-1.0	0.0	4.1	-3.9	-5.0	-3.0
	BS2	9.0	4.9	-0.9	0.1	4.1	-3.8	-4.9	-3.0
	BS3	8.9	4.8	-0.8	0.1	4.2	-3.9	-4.8	-2.9
MP2	BS1	8.6	4.4	-0.6	-0.1	4.1	-3.6	-4.8	-3.0
	BS2	8.5	4.4	-0.6	0.0	4.1	-3.6	-4.6	-2.9
	BS3	8.5	4.4	-0.6	-0.1	4.0	-3.6	-4.7	-2.9
QCISD	BS1	8.6	4.7	-0.7	0.0	4.0	-3.7	-4.8	-3.0
	BS2	8.5	4.7	-0.7	0.1	3.9	-3.7	-4.7	-3.0
BVWN	BS1	8.2	4.3	-0.3	0.0	4.0	-3.4	-4.5	-2.6
	BS2	8.2	4.2	-0.3	0.1	4.0	-3.4	-4.3	-2.5
	BS3	8.1	4.1	-0.2	0.2	4.1	-3.4	-4.3	-2.5
BLYP	BS1	8.1	4.3	-0.3	0.1	3.9	-3.4	-4.4	-2.6
	BS2	8.0	4.2	-0.3	0.1	3.9	-3.4	-4.3	-2.5
	BS3	7.9	4.1	-0.3	0.2	4.0	-3.4	-4.2	-2.4
B3LYP	BS1	8.4	4.4	-0.5	0.1	4.0	-3.6	-4.6	-2.7
	BS2	8.3	4.4	-0.5	0.1	4.0	-3.5	-4.4	-2.6
	BS3	8.2	4.3	-0.4	0.2	4.1	-3.5	-4.4	-2.6

^aThe energies are given in kilocalories per mole.**TABLE IX.**
Energies and Corrections for GAUSSIAN-1 and GAUSSIAN-2 Theory.^a

Species	MP4 / 6-311G**	$\Delta E(+)$	$\Delta E(2df)$	$\Delta E(QCI)$	$\Delta E(HLC)$	$\Delta E(ZPE)^b$	$\Delta E(TE)^{b,c}$	$\Delta G2$
CF ₃ ·	-336.97036	-17.39	-174.69	2.84	-73.87	11.98	15.28	-16.03
H·	-0.49981	0.00	0.00	0.00	-0.19	0.00	1.42	0.00
CF ₃ H	-337.64593	-17.98	-175.18	3.45	-79.82	25.15	28.46	-18.04
OH·	-75.58825	-7.09	-35.36	-0.96	-18.61	8.19	10.46	-5.19
CF ₃ OH	-412.74434	-20.73	-217.11	4.58	-98.24	28.33	32.54	-22.68
H ₂	-1.16772	0.00	0.00	-0.59	-6.14	9.93	12.20	-2.49
H ₂ O	-76.27607	-10.83	-37.39	0.00	-24.56	20.64	23.37	-8.27
F ₂ C=O	-312.45758	-14.39	-165.49	6.24	-73.68	13.63	16.80	-14.22
HF	-100.27374	-12.09	-45.88	0.28	-24.56	8.85	11.12	-7.44
CF ₂ :	-237.27823	-12.28	-121.52	2.41	-55.26	6.85	9.72	-11.15
F·	-99.56534	-5.78	-42.56	-0.46	-18.61	0.00	1.42	-3.49
TS3	-338.11683	-17.69	-174.94	1.50	-80.01	22.42	26.61	-18.73
TS4	-413.21595	-24.41	-212.38	-0.18	-98.43	29.88	35.56	-23.49
TS5	-413.16907	-26.72	-215.83	-0.45	-98.43	29.53	34.75	-22.28
TS9	-337.52240	-22.55	-173.10	6.11	-79.82	18.01	21.82	-18.00
TS10	-412.66948	-21.02	-217.37	7.76	-98.24	22.88	26.96	-21.82

^aEnergies in hartrees; corrections in millihartrees.^bCalculated by MP2 / 6-31G* level and scaled by 0.961.^cThermal energy corrections at 298.15 K.

TABLE X.
Activation Energies and Heats of Reactions Calculated by GAUSSIAN-1 and GAUSSIAN-2 Theory and Individual Methods Needed for Them.

Reaction	MP2 ^a	MP4 ^b	t ^c	2df ^d	QCISD ^e	+3df ^f	G1	G2
Activation energy (kcal / mol)								
3	25.0	16.4	16.5	16.5	15.1	19.8	15.5	15.1
4	13.3	9.2	9.6	8.0	7.5	9.1	6.9	6.7
5	57.4	47.9	44.1	48.7	44.7	49.9	41.8	42.0
7	80.3	72.8	70.0	74.2	74.5	75.0	73.1	73.2
8	43.9	43.4	43.2	43.3	45.4	43.9	45.2	45.8
Heat of reaction (kcal / mol)								
1	-96.4	-103.2	-103.5	-103.5	-102.8	-103.4	-107.4	-108.0
2	-118.3	-112.7	-110.3	-117.1	-111.0	-120.4	-116.9	-117.1
3	9.3	3.3	3.6	3.6	2.5	6.6	3.2	2.9
4	-8.2	-7.9	-9.8	-8.8	-7.6	-15.7	-10.6	-11.3
5	13.7	1.7	-3.0	4.8	0.6	1.3	-1.1	-2.1
6	89.6	77.4	77.0	84.1	76.9	92.6	83.2	84.1
7	67.4	54.6	50.6	59.5	54.1	58.3	55.2	54.8
8	12.8	5.7	2.1	9.3	7.0	5.9	7.1	7.7

^aMP2(FU) / 6-31G* // MP2(FU) / 6-31G*.
^bMP4 / 6-311G** // MP2(FU) / 6-31G*.
^cMP4 / 6-311 + G** // MP2(FU) / 6-31G*.
^dMP4 / 6-311G**(2df) // MP2(FU) / 6-31G*.
^eQCISD(T) / 6-311G** // MP2(FU) / 6-31G*.
^fMP2 / 6-311 + G(3df, 2p) // MP2(FU) / 6-31G*.

The effect of scaling factors on the activation energies or the heats of reactions were negligibly small.

GAUSSIAN-1 and GAUSSIAN-2 theory gave the best results in regard to both activation energies and heats of reactions.

Supplementary Material

Tables are available as Supplementary Material.

Acknowledgments

We thank Research Information Processing System Station of the Agency of Industrial Science and Technology for providing computational resources. We also thank Drs. Wasada and Tsutsui for providing the MOLCAT program,²⁹ which is a visualizing software of the GAUSSIAN output file.

References

1. M. J. Molina and F. S. Rowland, *Nature* **249**, 810 (1974).
2. W. A. Rosser, H. Wise, and J. Miller, *Symp. (Int.) Combust., [Proc.]*, 7th, 175 (1959).

3. C. K. Westbrook, *Symp. (Int.) Combust., [Proc.]*, 19th, 127 (1982).
4. H. Fukaya, E. Hayashi, Y. Hayakawa, H. Baba, H. Taoda, T. Osaki, and T. Abe, *J. Environ. Chem.*, **3**, 271 (1993).
5. K. Takahashi, Y. Sekiuiji, T. Inomata, T. Abe, H. Fukaya, E. Hayashi, and G. Inoue, *Combustion Sci. Technol.*, **102**, 213 (1995).
6. H. Fukaya, T. Ono, and T. Abe, *J. Chem. Soc., Chem. Commun.*, 1207 (1994).
7. (a) J. S. Francisco, *Chem. Phys.*, **150**, 19 (1991); (b) J. S. Francisco, *Chem. Phys. Lett.*, **218**, 401 (1994); (c) Y. Fu, W. Lewis-Began, and J. Tyrrel, *J. Phys. Chem.*, **99**, 630 (1995).
8. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, GAUSSIAN-92, Revision G.1, Gaussian Inc., Pittsburgh, PA, 1992.
9. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefano, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, GAUSSIAN-94, Revision B.3 or D.4, Gaussian Inc., Pittsburgh, PA, 1995.
10. O. N. Ventura, M. Kieninger, and E. L. Coitiño, *J. Comput. Chem.*, **17**, 1309 (1996).

11. C. Møller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).
12. A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988).
13. S. H. Vosko, L. Wilk, and M. Nussair, *Can. J. Phys.*, **58**, 1200 (1980).
14. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
15. A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
16. (a) J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.*, **90**, 5622 (1989); (b) L. A. Curtiss, G. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.*, **93**, 2537 (1990).
17. L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.*, **94**, 7221 (1991).
18. There are other possible reactions in the combustion zone; for example, the reaction of $\text{CF}_3 \cdot$ with O_2 and combustible material and that of CF_2 with $\text{H} \cdot$, $\text{OH} \cdot$, and $\text{CF}_3 \cdot$. The study on these reactions is in progress.
19. M. W. Chase Jr., C. A. Davies, J. R. Downey Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables, 3rd Ed.*, *J. Phys. Chem. Ref. Data*, **14** (Suppl. 1) (1985).
20. A. R. Hoy and P. R. Bunker, *J. Mol. Spectrosc.*, **74**, 1 (1979).
21. Appear in Supplementary Material.
22. A. P. Scott and L. Radom, *J. Phys. Chem.*, **100**, 16502 (1996).
23. M. W. Wong, *Chem. Phys. Lett.*, **256**, 391 (1996).
24. C. W. Bauschlicher Jr. and H. Partridge, *J. Chem. Phys.*, **103**, 1788 (1995).
25. L. J. Chyall and R. R. Squires, *J. Phys. Chem.*, **100**, 16435 (1996).
26. S. G. Lias, Z. Karpas, and J. F. Liebman, *J. Am. Chem. Soc.*, **107**, 6089 (1985).
27. P. Gray, A. A. Herod, and A. Jones, *Chem. Rev.*, **71**, 247 (1971).
28. (a) C. J. Howard and K. M. Evenson, *J. Chem. Phys.*, **64**, 197 (1976); (b) J. Ernst, H. G. Wagner, and R. Zellner, *Ber. Bunsenges. Phys. Chem.*, **82**, 409 (1978); (c) K. Jeong and F. Kaufman, *J. Phys. Chem.*, **86**, 1808 (1982); (d) A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S. A. McKeen, and A. R. Ravishankara, *J. Phys. Chem.*, **97**, 8976 (1993).
29. Y. Tsutsui and H. Wasada, *Chem. Lett.*, 1995, 517; JCPE Program No. P109.